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September 17, 2004

Dr. Harin Ullal, MS3212 National Center for Photovoltaics National Renewable Energy Laboratory 1617 Cole Blvd Golden, CO 80401

Re: Thirty-third Monthly Report #NDJ-2-30630-11

Dear Harin,

This letter comprises the monthly technical status report for ITN's subcontract # NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. The reported work was performed during the ninth month of phase 3 for this contract (thirty-third month overall), which is August 7, 2004 through September 7, 2004. This report describes activities performed by ITN, as well as those performed by lower-tier subcontractor Colorado School of Mines (CSM), under the direction of Dr. Colin Wolden.

## 1. Program Goals and Approach

Our primary objective under this program is to determine if the chalcogen in CIGS coevaporation can be delivered more effectively by activation with a plasma. Possible advantages of plasma-assisted co-evaporation (PACE) are

- increased utilization of chalcogens,
- decreased deposition temperatures,
- decreased deposition times, and
- increased ability to tailor S/Se ratio.

University researchers at CSM are developing and testing the fundamental chemistry and engineering principles. Industrial researchers at ITN are adapting PACE technology to CIGSS co-evaporation and validating PACE process for fabrication of thin film PV. In<sub>2</sub>Se<sub>3</sub> films, which are used as precursor layers in high-efficiency CIGS depositions, were used as the first test case for the examining the advantages of PACE listed above, and significant advantages were demonstrated. Presently, the examination is being extended to the complete high-efficiency three-stage CIGS co-evaporation process.

## 2. Incorporation of PACE Sources Into Three-Stage Deposition

This month, for the first time, plasma-activated Se was delivered to the substrate at rates commensurate with co-evaporation, in the three-stage CIGS co-evaporation chamber. Plasma-activated Se was delivered at a plasma power of 100 W and rate of 25 Å/sec. This rate was maintained for approximately the time of a CIGS deposition without evidence of Se condensation in the plasma tube or difficulty maintaining the plasma. Several iterations of the PACE source installation were necessary before the desired rate was obtained. It was found that

- Higher tube pressures ( $\geq$ 500 mT Ar) and plasma powers ( $\geq$ 60 W) are helpful in preventing coating of the quartz plasma tube with Se and preventing the plasma from vanishing into the neck of the tube.
- Chiller water temperature of 50, rather than 20, °C supplied to the RF coil also helps prevent tube coating.
- The tube should be wrapped with several layers of fiber glass to keep Ar away from the RF coil, thereby keeping the plasma confined to the inside of the reactor tube.
- Metallic shielding should not be included, due to severe heating and subsequent shorting through the fiberglass to the RF coil.

The next deposition cycle will attempt three-stage CIGS co-evaporation with plasma activated Se.

## 3. Film Formation Studies

The benchtop source at CSM has been used to further the understanding of film formation during plasma-enhanced chalcogen exposure. It was demonstrated previously by x-ray diffraction (XRD) that Cu-In-Ga precursors could be completely converted to CIGS at 350 °C with plasma exposure, but not without. This month, the degree of conversion evident in the XRD was found to be associated with characteristic features in the morphology, as judged by scanning electron micrograph (SEM). Only fully-converted films exhibit a dense polycrystalline morphology, with well-defined grains.

This month, the benchtop source was also used to examine  $H_2S$  as a source material, instead of solid chalcogens. Amount of  $H_2S$  exposure was found to be easily regulated with standard gas flow controls. No evidence of condensation in the ICP apparatus was apparent, and optical emission shows that the  $H_2S$  dissociates readily in the plasma. Preliminary experiments using  $H_2S$  to convert metallic precursors to CIGS were conducted, and conversion –although not complete under the conditions tested to date – was observed.

## 4. Publications and Team Activities

A manuscript for the *Journal of Vacuum Science and Technology A* is being written. It will be submitted by October 1 in conjunction with the upcoming AVS meeting.

A manuscript for the fall SET meeting will also be written next month.

ITN and CSM participate in CIS team activities. This month, a first draft of a publication describing absorber sub-team activities was reviewed by all authors. Suggested revisions are being assembled into a second draft, to be distributed to participants shortly.

Best Wishes,

Ingrid Repins

Principal investigator ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services

Dr. Colin Wolden; CSM technical lead